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Amorphous Semiconductors

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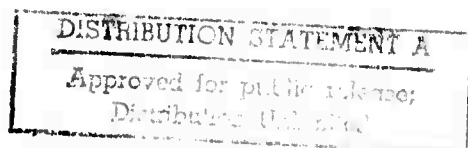
SUMMARY

Data have been taken on sound speed in Ge:Te: As alloys as a function of pressure and of temperature. Such data reveals the mechanical properties of the semiconducting glasses to be quite similar to those of conventional glasses. Measurement of pressure effects on dc resistivity confirm the earlier results of Fagen, et al.; ac experiments are incomplete at present. Correlations between the glass transition T_g and electrical activation reported by Krebs are used to predict the trend of T_g with pressure.

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NARRATIVE

The proposed research concerns the effects of pressure on amorphous semiconductors. Two broad areas were to be investigated experimentally: 1) the effect of temperature, pressure, and frequency on the electrical conductivity and 2) the effect of pressure on the speed of sound and the glass transition temperature. It now appears that the sound speed data will yield an equation of state as well.

The acoustic work has developed to the point that a brief paper was submitted to the Materials Research Bulletin, and will appear shortly. (Appendix A) Several points can be made comparing the semiconducting glass with more common ones. In sum, there is no real difference. The compressibility was found to <u>decrease</u> on compression at a rate of 2×10^{-13} cm^2/dyne/kbar and, while a few glasses[1] exhibit an increase in compressibility at low pressures, the general trend[2] is for the compressibility to decrease at a comparable rate. For example, the rate is 10^{-13} cm^2/dyne/kbar in 10% sodium borate.[3] Weir and Shartsis[3] have surveyed the alkali metal-borate system and find a decreasing pressure effect as the alkali content increases. Presumably the alkali ions fill holes in the structure, and the filled hole is less compressible than an empty one. The effect of a given ion (K^+ or Li^+, say) then depends on the availability of vacancies of an appropriate size. Our data do not presently cover a composition range sufficient for any trends to be seen. However, others have surveyed binaries such as S-As[4-6] and find, in that case a decrease in compressibility as As is added to S. One would infer that the effect of pressure would be less in the high-As glass, by analogy with the borate.

Our measurements, and indeed even common sense, contradict the report

by Kolomiets and Raspopova[7] that the bulk and shear moduli are identical. We find a ratio of bulk to shear close to <u>two</u>. The algebra goes as follows. The longitudinal velocity is given by $\rho v_\ell^2 = C_{11}$, and the transverse by $\rho v_s^2 = C_{44}$. For an isotropic material $2C_{44} = C_{11} - C_{12}$. Thus equal longitudinal and transverse speed require $C_{12} = -C_{11}$. Kolomiets and Raspopova however use $C_{11} = 3C_{12}$ in their analysis.

Six months ago we reported acoustic observation of the glass transition in <u>$Te_{15} Ge_3 As_2$</u>. While that experiment was satisfactory we have sin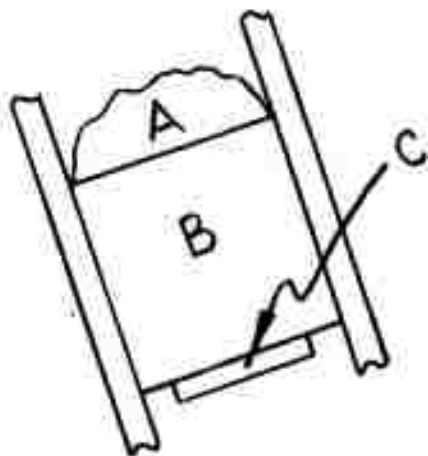ce gone to the system sketched in Fig. 1. The sample is an irregular lump A with only one polished face, where it joins the quartz delay line B. The transducer is at C. Sound waves propagate upward and are reflected at the A-B interface. Reflection at the top of the sample is unimportant because of the ir-regularities. Even if the sample melts, the top surface will not be parallel to the A-B interface because of the overall tilt of the delay line. The reflected signal strength is thus a function of impedance mismatch at AB. The change in compressibility at the glass transition T_g[8] will than produce a strong change in the reflected signal. When instrumentation is complete, both reflected signal and thermocouple emf will be applied to an x-y recorder for automatic recording of the event. A somewhat similar technique has been proposed by Heydeman and Houck.[9]

Sound speed data will continue to be taken in the present apparatus which requires a sample with two, accurately parallel, polished faces.

Figure 1

Such samples inevitably are considered to be more precious.

We have measured resistivity as a function of T, P and ω (frequency), but have not yet put all three variables together. The temperature data yield activation energies near those reported by Haisty and Krebs[10] and Fagen, et al.[11] We have extended the pressure data of Fagen, et al. to 10 kbar and find data as shown in Fig. 2. The resistivity has been measured using both Ag and carbon electrodes. The dashed lines are based on data obtained on this alloy by Fagen, et al. There is about an order-of-magnitude difference between the two results. However, the previous measurements were made on co-planar thin films whereas the present data are from measurements on bulk samples. Such differences are common. Note the apparent curvature in the present data. The analysis of the data requires that the conductivity activation energy ΔE be expanded in a power series of the form
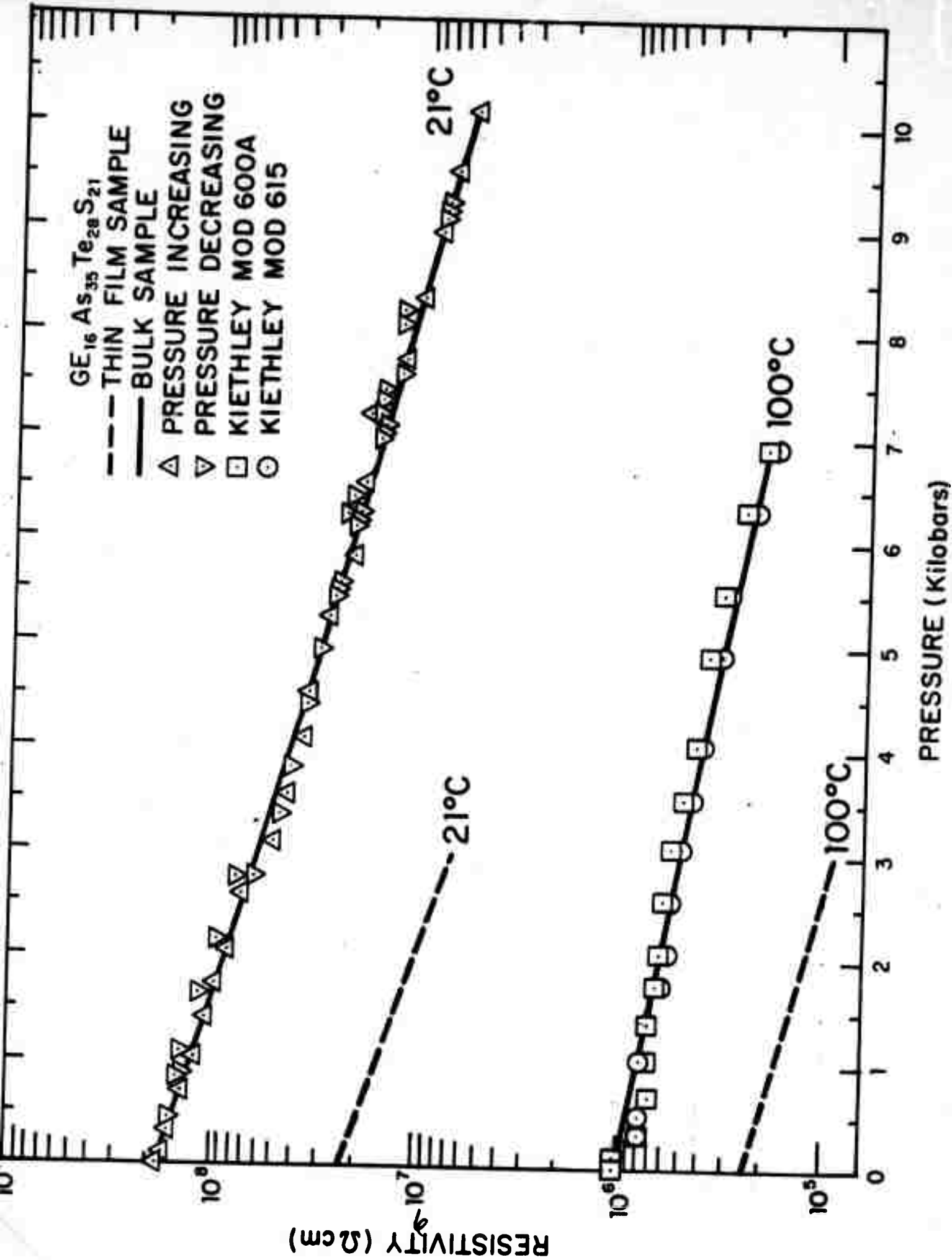
$$\Delta E = E_0 + E_1 T + E_2 T^2$$
$$+ E_1' P + E_2' P^2$$
$$+ E_2'' PT + \dots$$

The log derivative of the resistivity with respect to pressure is then

$$(kT)^{-1}[E_1' + 2E_2' P + E_2'' T + \dots]$$

Within our current precision $T \, \partial \ln \rho / \partial P$ is constant implying that E_2'' is negligible. E_1' is about 1.7×10^{-5} eV/bar. These results do not differ appreciably from those of Fagen, et al.[11]

The three samples studied thus far fail to show any frequency dependence to the resistivity presumably because the dc term dominates the ac term. The original motivation for this experiment was to attempt to separate hopping from band conduction contributions to electrical transport. Kolomiets and

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Figure showing resistivity versus pressure for $GE_{16}As_{35}Te_{28}S_{21}$ at $21°C$ and $100°C$.

Legend:
$GE_{16}As_{35}Te_{28}S_{21}$
— THIN FILM SAMPLE
— BULK SAMPLE
△ PRESSURE INCREASING
▽ PRESSURE DECREASING
□ KIETHLEY MOD 600A
⊙ KIETHLEY MOD 615

Y-axis: RESISTIVITY (Ω cm)
X-axis: PRESSURE (Kilobars)

co-workers[12], have recently reported an excellent experiment in this same direction. They studied $As_2 Se_3$ and $As_2 Te_3$: $As_2 Se_3$ alloy over the 0-4 kbar range. The two materials behave quite differently: the ac and dc conductivities of the pseudo-binary shift parallel with pressure, while the high frequency conductivity of $As_2 Se_3$ does not appear to depend on pressure. Thus one assumes the $As_2 Se_3$: $As_2 Te_3$ conduction to be due to free carriers in a band. The band separation goes down as pressure goes up. The absence of a pressure effect on the ac conductivity of $As_2 Se_3$ suggests that band parameters and carrier densities do not matter. Hopping between localized states would thus be the most probable conduction process. The absence of a pressure dependence for $As_2 Se_3$ can be attributed to a competition between an increasing activation for hopping and a decreasing hopping distance as pressure increases.

A recurrent problem in the theory of glasses is the nature and origin of the glass transition: that process in which the rapidly fluctuating disorder of a fluid is frozen into the rigid structure of a glass. It appears that amorphous semiconductors offer a unique insight into that process. Though the experiments reported here are as yet too few to be useful, there is adequate data in the literature to permit a speculation of considerable potential value. The data, due mainly to Krebs and his associates[13] are illustrated in Fig. 3 a-c. In Fig. 3a the glass forming regions of the Ge:Te:As alloy system are shown. Figures 3b and 3c show, respectively, the contours of constant glass transition temperatures T_g and constant electrical activation energy ΔE. There is a striking parallelism between the trends in T_g and ΔE, particularly when one considers the intrinsic uncertainties in each quantity. (We hope to remove some of these uncertainties in the present work.) Clearly T_g and ΔE are related, in this system at least. The two, at first glance dissimilar,
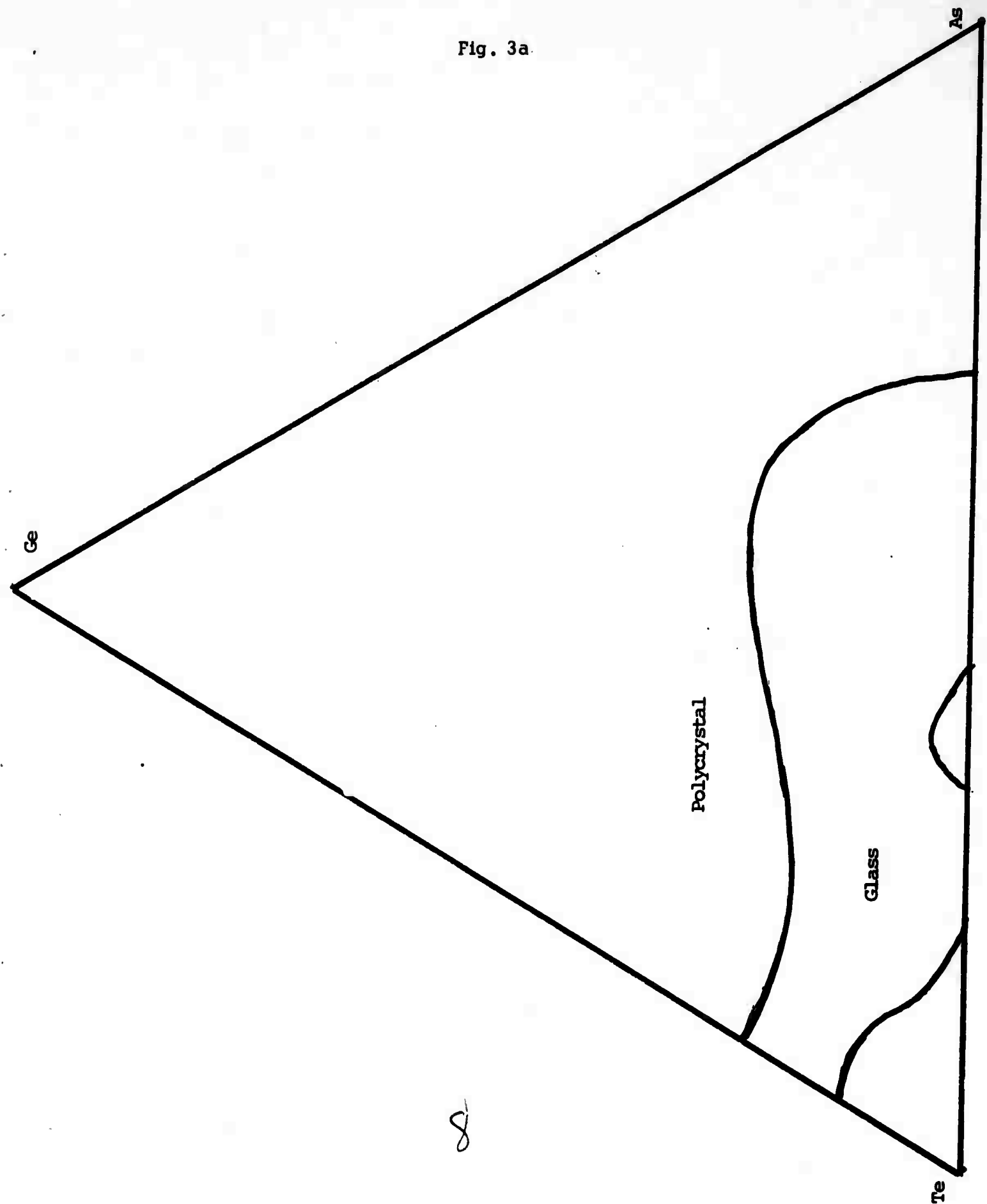
Fig. 3a

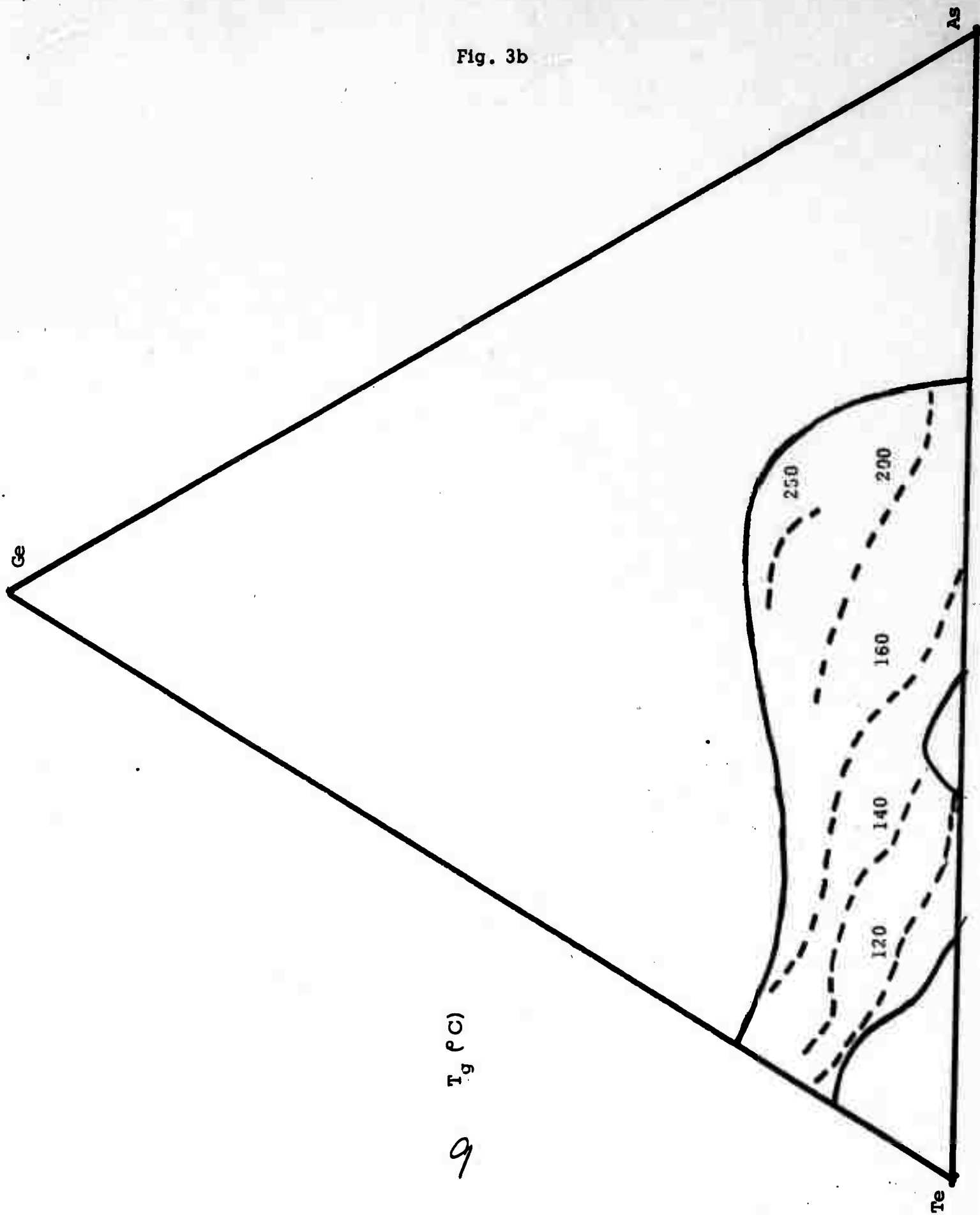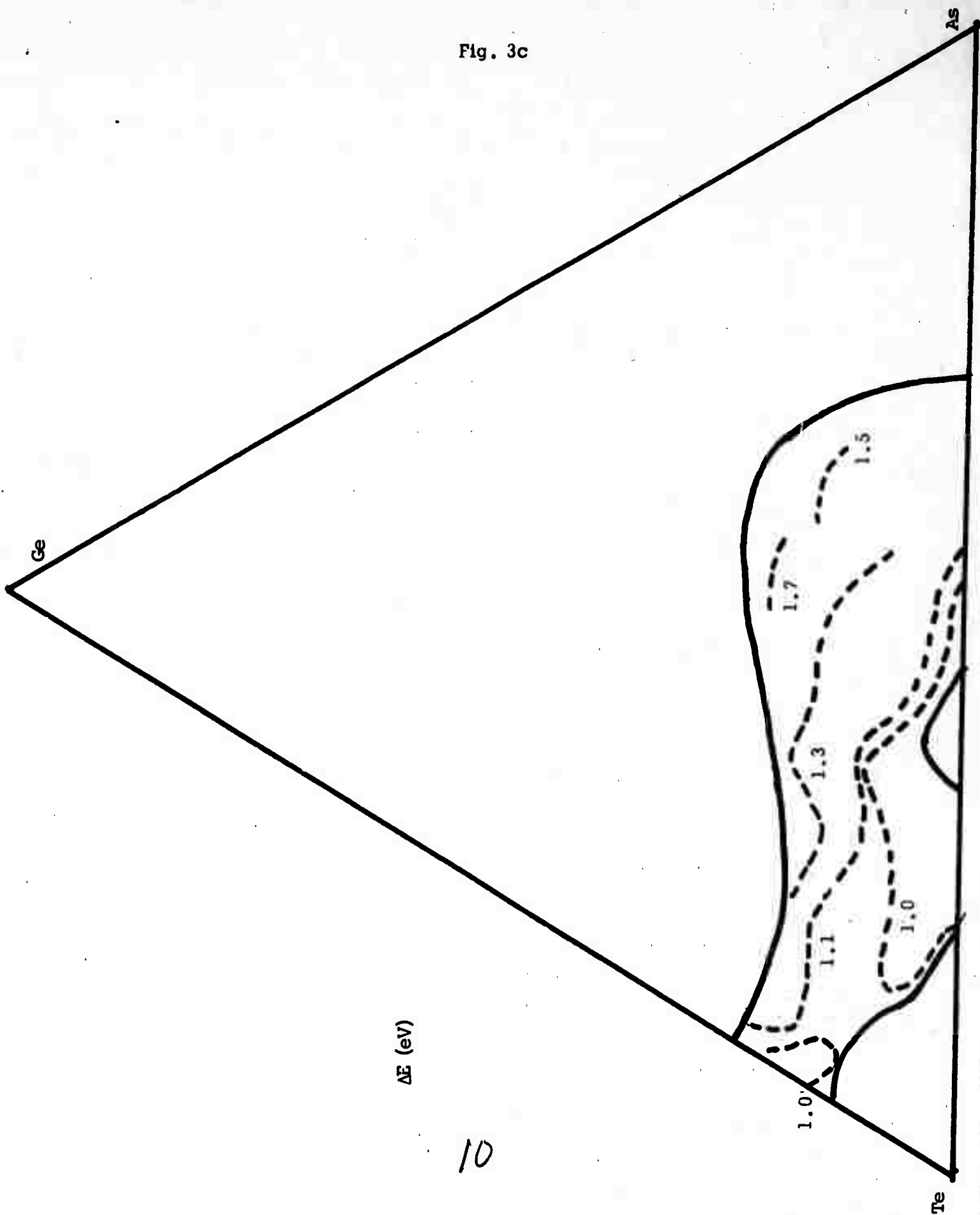Ge

As

Te

Polycrystal

Glass

Fig. 3b

T_g (°C)

9

Fig. 3c

10

parameters somehow gauge the same thing. I suggest that it is the free carrier density which is relevant. When thermal energies kT are a given fraction of ΔE then a given fraction of the valence band electrons are excited into the conduction band. The vacant bonds left behind weaken the material and permit the atomic motions which are a part of the liquid, as opposed to glassy, state. T_g is then seen to be a function of ΔE. If ΔE is reduced, as by increased pressure, then T_g will decrease as well. Thus amorphous semiconductors are predicted to show a negative dT_g/dP, in contrast to more common glasses.[14] When the free carrier density is increased over thermal equilibrium values, as by photons with energy above the band gap, T_g would be expected to decrease. Such an expectation is consistent with the laser-enhanced crystallization rate observed by Feinleib,[15] since crystallization can only occur above T_g. Further confirmation that free carriers and the concomitant broken bonds enhance atomic motions is provided by the Se crystallization studies of Dresner and Stringfellow.[16] However, lone pair semiconductors[17] should not behave like the tetrahedrally bonded semiconductors discussed here since carrier activation does not imply bond breaking. The ramifications for glass transition in general or for switching in amorphous semiconductors have yet to be explored.

In summary we note substantial progress toward each of the goals of the program, but as yet the coherent study of several samples has not been attained. Such study should be achieved during the next half year.

There is, however, an impending move from the present Physics building to a new structure. Since the entire department is involved and since the space to be occupied grosses at over 150,000 sq. ft., the move is an enormous effort. There will be an unavoidable loss of time and efficiency. The move was originally scheduled for September 1971, and should have been over before we reached the current level of activity.

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Amorphous Semiconductors

Pressure Studies in Chalcogenide Alloys*

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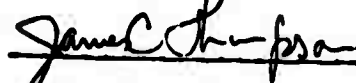J.C. THOMPSON, University of Texas at Austin-

Sound speed and electrical resistivity have
been measured at hydrostatic pressures to
10 kbar in glassy Ge:Te:As alloys. Cook's
analysis was used to eliminate sample
compression effects on the acoustic transit
time so that the sound speed could be cal-
culated. The speed increases with P. The
log of the resistivity is a non-linearly
decreasing function of P. The influence of
temperature and composition will be
reported.

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PRESSURE EFFECTS ON SOUND IN GLASSY SEMICONDUCTORS*

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Revised

ABSTRACT

The speed of ultrasonic waves has been measured in glassy $Te_{15}Ge_3As_2$ under hydrostatic pressure up to 10 k bar. Cook's analysis was used to eliminate sample compression effects on the acoustic transit time so that sound speed could be calculated. The sound speed increases smoothly with increasing pressure. The compressibility varies from 5.66×10^{-12} cm^2/dyne at one atmosphere of pressure to 3.86×10^{-12} cm^2/dyne at 10 k bar. The isothermal compressibility, Debye temperature, Grüneisen parameter, density, Young's modulus, shear modulus, and Poisson's ratio have been calculated from the acoustic data and are tabulated.

Introduction

The speed of ultrasound has been investigated in the bulk alloy glass $Te_{15}Ge_3As_2$ under hydrostatic pressure at room temperature. The actual experimental parameter is the transit time of a short pulse of ultrasonic waves in a cylindrically shaped sample. Conversion of the measured transit time to sound speed requires a knowledge of the change in sample length with pressure. This change in sample length is determined using the method of Cook (1), described below. Assuming equal compressibility in all directions, as expected for a glass (2), κ_T, the isothermal compressibility is related to the adiabatic compressibility, κ_s, by

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$$\kappa_T \equiv \frac{-3}{\ell} \frac{\partial \ell}{\partial P}\Big)_T = \gamma \kappa_s \equiv \frac{-3\gamma}{\ell} \frac{\partial \ell}{\partial P}\Big)_s, \tag{1}$$

where ℓ is the length of the sample and γ is the ratio of specific heats. If the initial length and density are ℓ_0 and ρ_0 respectively then the sample length and density under pressure are described by

$$\ell(P) = \frac{\ell_0}{y(P)} \quad \text{and} \quad \rho(P) = y(P)^3 \rho_0. \tag{2}$$

The function $y(P)$, the ratio of the initial length to the length under pressure, is always equal to or greater than unity. The longitudinal and transverse sound velocities are given by

$$v_\ell^2 = \frac{1}{\ell}\left(\frac{1}{\kappa_s} + \frac{4}{3}\mu_s\right) = \frac{\ell_0^2}{y^2 t_\ell^2} \tag{3}$$

and

$$v_t^2 = \frac{\mu_s}{\rho} = \frac{\ell_0^2}{y^2 t_t^2}, \tag{4}$$

where μ_s is the shear modulus; t_ℓ and t_t are the longitudinal and transverse transit times respectively.

Upon combining equations (2) - (4) the function $y(P)$ can be expressed in terms of the experimental parameters by

$$y(P) = 1 + \frac{\gamma}{3\rho_0 \ell_0^2} \int_0^P \left(\frac{1}{t_\ell^2} - \frac{4}{3}\frac{1}{t_t^2}\right)^{-1} dp. \tag{5}$$

The longitudinal and transverse transit times were found to satisfy Eqs. (6) and (7), respectively

$$t_\ell = C_1 P^2 + C_2 P + C_3, \tag{6}$$

$$t_t = t_\ell (C_4 P + C_5). \tag{7}$$

These equations are chosen as a convenience in performing the integration in Eq. (5). The C's are empirical constants. With the function $y(P)$ known, the compressibility of the material can be calculated from Eqs. (3) and (4).

Experimental

The Te:Ge:As alloy was formed by maintaining the material in the molten

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$$\kappa_T \equiv \frac{-3}{\ell} \left.\frac{\partial \ell}{\partial P}\right)_T = \gamma \kappa_s \equiv \frac{-3\gamma}{\ell} \left.\frac{\partial \ell}{\partial P}\right)_s, \tag{1}$$

where ℓ is the length of the sample and γ is the ratio of specific heats. If the initial length and density are ℓ_0 and ρ_0 respectively then the sample length and density under pressure are described by

$$\ell(P) = \frac{\ell_0}{y(P)} \quad \text{and} \quad \rho(P) = y(P)^3 \rho_0. \tag{2}$$

The function $y(P)$, the ratio of the initial length to the length under pressure, is always equal to or greater than unity. The longitudinal and transverse sound velocities are given by

$$v_\ell^2 = \frac{1}{\ell} \left(\frac{1}{\kappa_s} + \frac{4}{3} \mu_s \right) = \frac{\ell_0^2}{y^2 t_\ell^2} \tag{3}$$

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Experimental

The Te:Ge:As alloy was formed by maintaining the material in the molten

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state for 24 hours and then quenching
into a brine solution. The transit
times of both longitudinal and trans-
verse 10 MHz ultrasonic waves were
measured using a modified pulse-echo
technique (3), at pressures up to
10 k bar. The pressure device used was
a modified 30 k bar apparatus of the
Bridgman type (4), with nitrogen gas as
the pressure medium.

Results

The transit time data are shown
in Fig. 1, as a function of pressure.
The data in the upper part of the
graph are the transverse transit
times, which were taken up to 6 k bar
and the dotted line is an extrapola-
tion from Eq. (7). The longitudinal
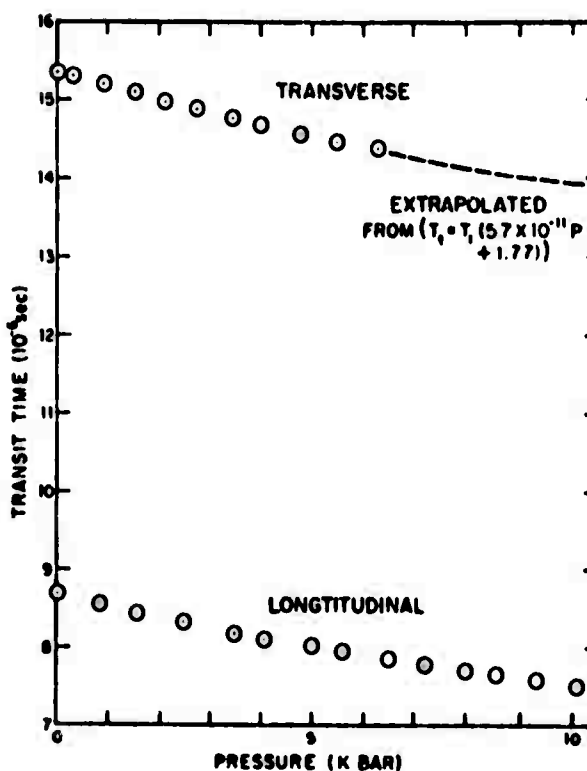transit times are shown in the lower
part of the graph.

FIG. 1

Measured Transit Times

Figure 2 shows the longitudinal sound velocity calculated for several
assumed values of γ. The upper curve is the velocity for $\gamma = 1.0$, the
second for $\gamma = 1.2$, the third for $\gamma = 1.4$ and the lower curve for $\gamma = 1.6$. γ
does not affect the sound velocity appreciably and the velocity varies
smoothly over the entire pressure range. These results are consistent with
those reported by Bowen at atmospheric pressure (5). The compressibility,
however, is affected to a much greater degree by variations in γ.

Fig. 3 shows the isothermal compressibility calculated for the same val-
ues of γ as in Fig. 2. Here the lower curve corresponds to $\gamma = 1.0$, next 1.2,
1.4 and 1.6. It must be pointed out that, as in most solids, γ is expected
to be very close to unity for these glasses. For example, in vitreous silica,
$1.000 < \gamma < 1.001$ (1). The actual value of the compressibility should there-
fore be very close to that shown in the lower curve in Fig. 3. We thus find
that κ_T is 5.66×10^{-12} cm^2/dyne at zero pressure and the pressure derivative
varies smoothly from -2.68×10^{-13} cm^2/dyne/k bar at zero pressure to $-1.15 \times$
10^{-13} cm^2/dyne/k bar at 10 k bar. The shear modulus has also been determined
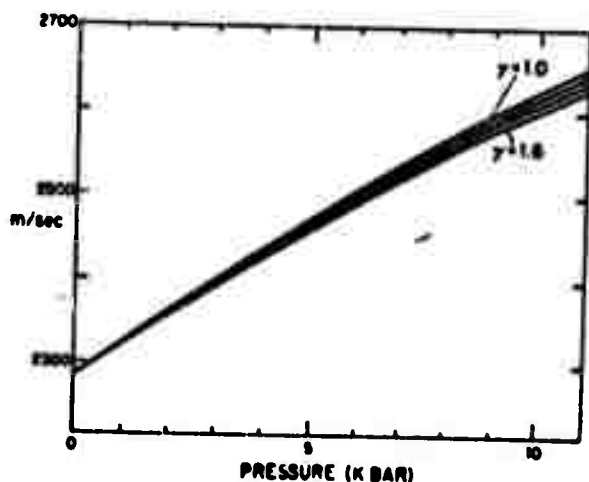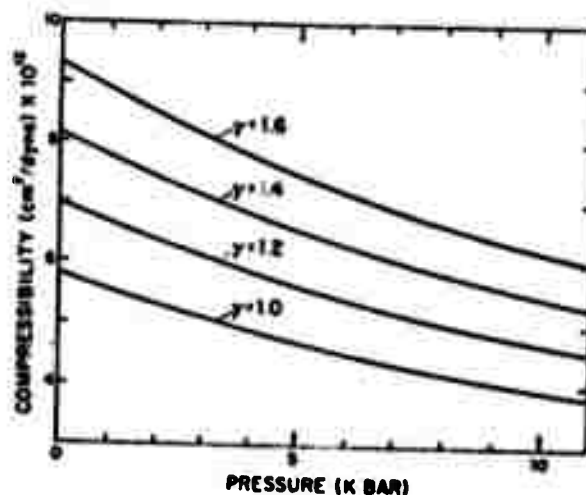
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FIG. 2

Longitudinal Sound Velocity

FIG. 3

Isothermal Compressibility

and is 9.6×10^{10} dynes/cm^2 at zero pressure. The pressure derivative varies smoothly from 2.79×10^9 dynes/cm^2/k bar to 1.82×10^9 dynes/cm^2/k bar. The volume change at 10 k bar is only 4.6%, which is very close to the value for vitreous boron oxide (6).

The decrease in κ_T with increasing pressure is to be expected since the atoms resist compression more strongly as they are pushed together (8); though the common glasses (pyrex and vitreous silica) are anomalous in that κ_T goes up with pressure at low pressures (7). The general and expected trend matches our observation.

TABLE 1

Mechanical Properties

	ρ g/cm^3	$Y \times 10^{-11}$ dyne/cm^2	$\mu \times 10^{-11}$ dyne/cm^2	σ	$\kappa_T \times 10^{12}$ cm^2/dyne	Ref.
Te$_{15}$Ge$_3$As$_2$	5.77	2.44	0.96	.27	5.66	this work
Pyrex	3.22	6.2	2.5	.24	2.52	8
Fused Quartz	2.2	7.29	3.12	.17	2.72	8
Al	2.70	7.24	2.71	.37	1.36	9
Mo	10.19	33.4	11.8	.35	0.36	9

Several other mechanical properties have been calculated from the acoustic data. The Debye temperature, which is independent of γ, is 117K at atmospheric pressure. The Grüneisen parameter is approximately 2.4.

Table 1 shows a comparison of some of the mechanical properties of the Te:Ge:As alloy with those of pyrex and fused quartz (8,9). The parameters are expressed in c.g.s. units.

The density, ρ, Young's modulus, Y, shear modulus, μ, Poisson's ratio, σ, and the isothermal compressibilities, κ_T, are tabulated. As can be seen from the table, the mechanical properties of the glasses are quite similar and give no hint of the enormous difference in their electrical properties (2). The authors wish to acknowledge the assistance and suggestions given in private communication by Dr. F. C. Sawin.

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